

Examining the Role of Quinone Moieties in the Photochemistry of Colored Dissolved Organic Matter in Coastal Waters

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LONG-TERM GOALS

My long-term goals are to develop an understanding of the photochemical processes affecting CDOM, and the resultant changes in its optical properties and molecular composition, particularly in coastal environments.

OBJECTIVES

CDOM is the most important sunlight-absorbing dissolved substance in the sea and a critical component of the global carbon cycle. Irradiated CDOM produces reactive species that interact in the ocean in a complex series of photochemical and electron transfer reactions that impact the color and oxidative capacity of surface waters, the growth of marine biota, and the production of volatile gases that impact climate. The identity of the key structural moiety in CDOM that absorbs sunlight and initiates this important cycling is unknown, but quinones have recently been hypothesized as likely candidates. The goal of this proposal is to investigate the structural features of CDOM associated with the photochemical formation of these reactive species, with the objectives of testing the quinone hypothesis and examining photochemical transformations of the optical and structural properties of CDOM in river and coastal waters.

APPROACH

My approach is to combine NMR techniques for structural characterization, along with measurements of photochemical products, to correlate specific structural features with enhanced photochemical activity and determine if quinone functionalities are the key feature in CDOM that absorbs sunlight and produces transient products such as peroxide. Thus, the experimental approach combines photochemical experiments, separation of CDOM fractions by ultrafiltration, and structural characterization by ^1H FT-NMR techniques. The acquisition and interpretation of NMR spectra of a complex material such as DOM is difficult. Dr. AJ Shaka, an NMR specialist in the Dept. of Chemistry at UC Irvine, and Kristin Cano, one of his graduate students, are collaborating on the NMR studies. Hydrogen peroxide is used as the “tracer” photochemical product for CDOM, since this compound is a direct photoproduct of irradiated quinones. One previous study correlated the presence of ketonic functionalities with CO production, an indirect photoproduct (Stubbins et al., 2000). Hydrogen peroxide is measured by a fluorescent enzyme-based method (Moore et al., 1993).

Common structural features associated with high H_2O_2 yields will be identified to test the quinone hypothesis. Relative absorbance, fluorescence and apparent quantum yields of photoredox products

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from different source materials (river vs. coastal) and sized fractions will be compared with relative functional group distributions from NMR studies to correlate particular structural features with photoredox production, and hence probe the chemical characteristics of the active redox site. Initial experiments will focus on the relative abundance of quinonoid moieties in the total CDOM mass as deduced from integration of ¹H NMR spectra.

If different CDOM size fractions have similar H₂O₂ yields, this would indicate that the active redox centers are evenly distributed throughout the humic material. By running the same size fractions by FT-NMR, we can estimate the relative number of quinone moieties associated with high photoproduct yields. Since studies with field flow fractionation and LC/MSⁿ techniques have shown differences between marine and freshwater DOM due to structural changes associated with photodegradation reactions, I will also examine how these structural features change with photochemical transformation processes in model time-course photochemical experiments on seawater samples in the laboratory.

WORK COMPLETED

In the first year of this grant, the major instrumentation was installed (Bruker 300 MHz FT-NMR, Agilent UV-VIS spectrometer, Photon Technology 3-D fluorometer, Turner 10AU field fluorometer, Turner TDS 2020 luminometer, Separation Engineering ultrafiltration system, Shimadzu TOC).

Methodology was developed through preliminary experiments with standard compounds (a series of six commercial quinones as simple models). At the end of this second year, photochemical work has been completed on commercial Aldrich humic and fulvic acids, a brown seaweed plant leachate, and 18 natural water samples (3 size fractions from 6 sites). With work completed on the simple model quinone compounds, much progress was made this year with the natural water samples. Samples from 5 local Southern California sites were collected and fractioned by ultrafiltration (1000 Dalton membrane). These sites included coastal waters and input river sources at area beaches (Doheny State Beach, Huntington State Beach), shelf waters and wetland production input areas (Newport Back Bay, Bolsa Chica). In addition, samples from the extensively studied Shark River in Southwest Florida were also extracted and analysed. Data collected from the photochemical studies include H₂O₂ measurements (kinetics and quantum yields), pre- and post-irradiation absorbance spectra and fluorescence spectra, and total organic carbon (TOC) measurements. For the determination of quantum yields, actinometric measurements of the 300W Xenon lamp output were made with a potassium ferioxalate chemical actinometer (Calvert and Pitts, 1966). The majority of progress has been in the area of ¹H NMR spectra. Methodology was developed in consultation with Dan Repeta (WHOI) to extract DOM from water samples for NMR analyses. Through collaboration with the Shaka Group at UCI, a successful NMR pulse program has been written that specifically addresses the needs of DOM extracts. These samples necessitated a program that would simultaneously suppress 2 solvent peaks and be sensitive to the variety and concentration of functionalities present in DOM. To date, the extractions and spectral acquisitions have been better than anticipated. Currently the NMR work is focusing on manipulation and interpretation of the spectra.

These findings were recently presented and a manuscript is in preparation for submission to Marine Chemistry:

J. G. Jones, C. D. Clark, D. E. Wellman, "Correlation of Photochemical Properties of Model Quinonoid Compounds and Colored Dissolved Organic Matter (CDOM) in Natural Waters", special session on photochemistry, ACS National Meeting, New Orleans, March 2003 (Session Chair Neil Blough).

RESULTS

Photochemistry: Upon irradiation, the DOM natural water samples and simple model quinines underwent photochemical reactions to produce H₂O₂. Typically, the natural water samples exhibit behaviors similar to the model compounds: H₂O₂ concentrations showed sharp initial increases, followed by periods of relative photochemical inactivity, and a concurrent decrease in absorbance with irradiation to give absorbance spectra similar to the characteristic CDOM spectrum (Figures 1 and 2). This is consistent with CDOM containing quinone moieties.

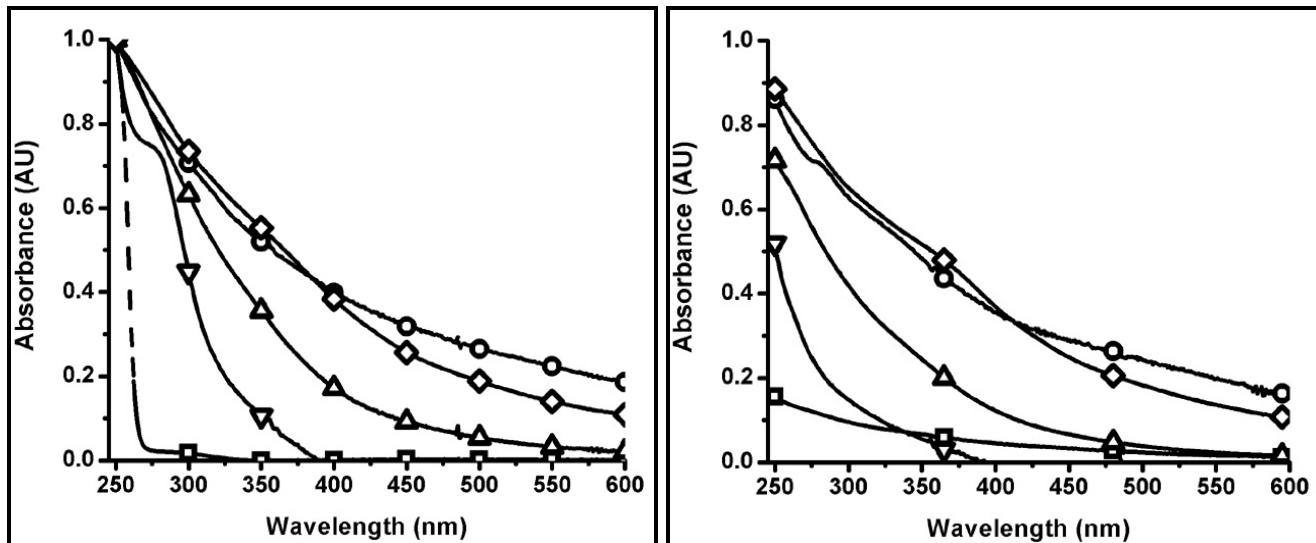


Figure 1. Left: Absorbance of model compounds and CDOM at $t = 0\text{ min}$. Absorbance corrected to 1.0 at 250 nm. (see legend in Figure 2) . Right: Absorbance after 60min irradiation (300W Xenon lamp); absorbance corrected by same factors as for $t = 0\text{ min}$. (Absorbance decreases from a maximum at 250 nm to a minimum at 600 nm).

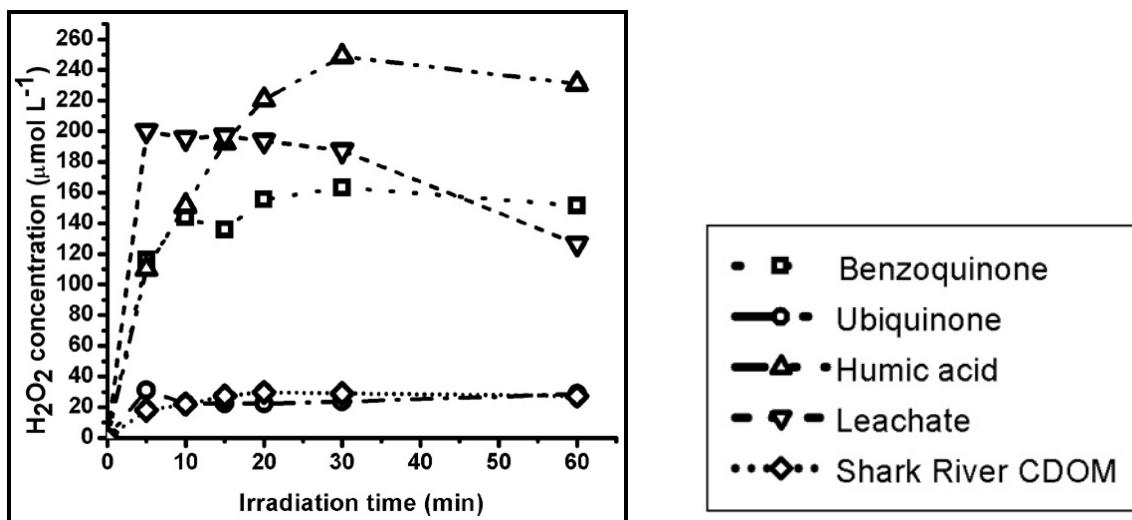


Figure 2. Hydrogen peroxide formation rates. [Concentrations increase from 0 $\mu\text{mol/L}$ at $t = 0\text{ min}$ to a maximum of ~20 to ~160 $\mu\text{mol/L}$ at 10 to 20 min for Shark River CDOM vs benzoquinone respectively; concentrations then remain fairly stable until the end of the irradiation at ~60 min]

The model compounds and natural water samples had similar peroxide formation curves, though values ranged over a factor of ~10; peroxide production curves were similar to those previously measured for bog DOM (Scully et al., 1996).

NMR Spectroscopy: The natural water samples have been size fractioned, irradiated, extracted, and NMR spectra have been acquired using a newly developed pulse program. The majority of the remaining work involves manipulation of the pre/post irradiation spectra, and the subsequent interpretation of these complex data sets.

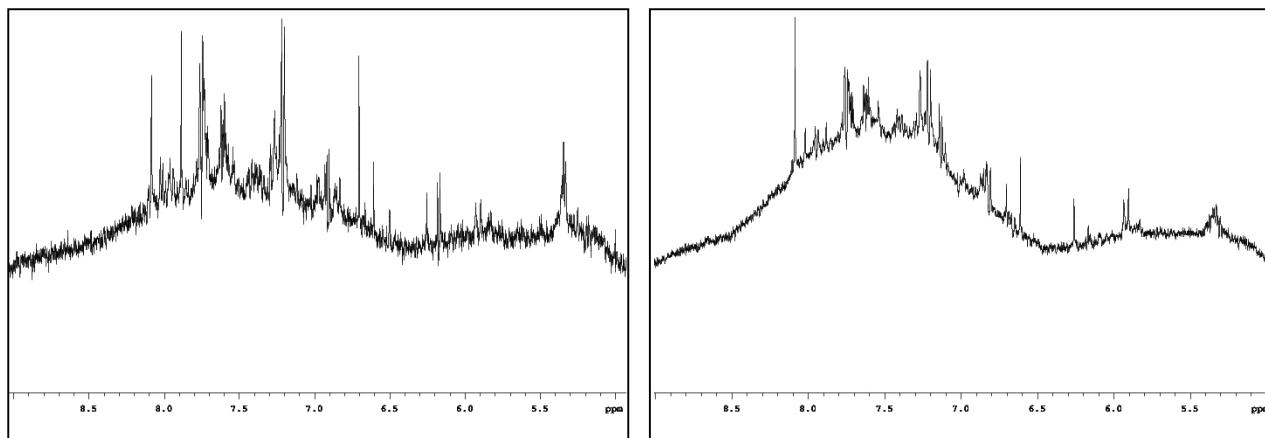


Figure 3. ^1H NMR spectra: Right: Doheney State Beach Creek CDOM > 1000 D.

Left: Doheney State Beach Creek CDOM < 1000 D (NMR spectra from 5 to 9 ppm showing two broad peaks overlaid with ~15-20 multiple peaks between 5 and 8 ppm; relative distributions of the peaks vary for the two size fractions with some additional peaks present in the <1000 Da fraction)

IMPACT/APPLICATIONS

Correlating photochemical activity with specific structural features in CDOM will allow us to develop better mathematical models for the attenuation of radiation in coastal environments. To really understand and model an optical process, we need to know the identity of the molecular chromophore, its concentration and its absorption coefficient. This work will contribute to a fuller understanding of the nature of the active sites responsible for the redox cycling and photochemical transformation of CDOM in sunlit waters, and hence the pathways by which the reactive species that impact ocean color, marine life and atmospheric composition are produced in the ocean.

RELATED PROJECTS

A library of coastal water samples continues to be accumulated in this laboratory for the optical and structural studies. Samples were collected for us on a recent cruise in the coastal waters of the Gulf of Mexico (Summer 2003, Bob Chen, Mississippi River).

Hydrogen peroxide measurements were made in a 24-hour diurnal mesocosm study of sewage indicator bacteria levels in coastal waters with microbiologists at Chapman University (January 2003). It has been hypothesized that the reduced levels of E. Coli in the surf zone during the day are caused by bacterial mortality due to increased levels of photochemically induced oxidizing agents in the surf

zone. However, the measured levels of ~400 nM were several orders of magnitude too low to directly induce bacterial mortality.

CDOM measurements were made in a multi-investigator interdisciplinary study at Doheney State Beach, CA, in the dry vs. wet season as a potential optical tracer for water mass sources at this highly polluted site (Nov 2002 to March 2003). A manuscript is in final preparation for submission to ES&T.

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